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# FRAME: An On-Line Correction Procedure for Quantitative Electron Probe Microanalysis

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# FRAME: An On-Line Correction Procedure for Quantitative Electron Probe Microanalysis

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A procedure using a mini-computer for on-line correction of x-ray data from electron microprobe analysis has been developed. This program, called FRAME, allows mass fractions to be computed on-line by the ZAF approach. Besides x-ray intensities, the only input data required are the atomic numbers of the elements present, the analytical line being used, and the operating voltage. Other required parameters such as atomic weights and x-ray mass attenuation coefficients are stored or calculated by the program. FRAME is in FORTRAN IV, and requires about 4K of computer core. Results from FRAME are very close to those of COR2, which is considered to be the most accurate program available for quantitative electron probe microanalysis.

Key Words: Electron probe; mini-computer; on-line correction; quantitative microanalysis.

## Introduction

The relative characteristic x-ray intensities measured with electron probe microanalyzers can be converted into concentrations of emitting elements, either by theoretical procedures, or by empirical calibration.

The theoretical procedures use generalized, though empirically adjusted expressions for the intensities of x-ray emission and absorption. They do not require, in principle, the use of any standards except elements, but they involve extensive calculation [1-3][1]. The empirical procedures, though simpler in calculation [4-5], usually require composite standards which may not be available in practice.

Electron probe microanalysis frequently consists of a sequence of measurements at various points on the specimen surface. In such case, it is useful to obtain the corrected results of the analysis at any point before deciding on the next step. Therefore, an on-line calculation procedure is desirable. However, such calculations were, in the past, available only for empirical data evaluation procedures [6].

This communication describes a correction procedure incorporated into a program (FRAME) which renders possible the on-line calculation with a minicomputer of concentrations (mass fractions) by the traditional ZAF approach [7].

## Evolution of the Program FRAME

The program MULTI8, developed by us and recently published [8], evaluates the experimental x-ray intensity lines by the theoretical method. MULTI8 can be used in a batch mode on a time-shared computer; it is similar to several programs now in use for such purposes in other laboratories. This program has the following limitations:

[1] Figures in brackets indicate the literature references at the end of this paper.

a. It omits the correction for fluorescence due to the continuum, and the integration over the range of energies of the electrons decelerating within the specimen in the calculation of generated primary x-ray intensities.

b. It requires, as part of the input, the mass absorption coefficients for all lines and elements and decisions concerning the applicability of fluorescence corrections for each line and element present.

c. The ZAF procedure requires the input of relative x-ray intensities corrected for detector dead-time and background. As MULTI8 does not contain provisions for these corrections, they must be performed externally before input.

A program such as MULTI8 would therefore be inadequate for on-line use, and its accuracy may be less than optimal under certain operating conditions. As it is more basic to obtain an accurate procedure than to apply it on-line, for the next step we developed a program, COR [3], which avoids, insofar as possible, all simplifications, and incorporates all correction steps known to us, including the correction for continuum fluorescence. Our aim was to obtain a benchmark, against which other programs could be compared. In effect, diverse correction formulae can be tested by substituting them into COR2, and the effects of simplifications, omissions, and empirical fits to partial correction steps can thus be evaluated.

The correction for the continuum fluorescence requires a fairly large computation. It was found expedient in the development of COR2 to calculate internally all x-ray mass absorption coefficients required for this correction; it was also necessary to divide the wavelength of the continuum range into regions confined by the absorption edges of the elements present in the specimen. Once these provisions were included, it was relatively simple to also determine internally which

corrections for fluorescence due to characteristic lines would apply in each case. We added an auxiliary sub-program to correct for background and dead-time, and we thus arrived at a rigorous procedure which requires a minimum of input — except for a table of constants which are kept in memory — and which is quite easy to handle in practical applications. Therefore, COR2, which was conceived primarily as a research tool, has proven to be very satisfactory for routine data calculation in the batch mode and is used extensively for this purpose at the National Bureau of Standards and in several other laboratories.

In the program FRAME, which is described here, we have incorporated into a simple model based upon MULTI8 the decision making and the internal calculation of parameters which were first developed for COR2. In this manner, we have obtained a program simple enough to be used on-line in a small computer. We have also included procedures to correct the observed x-ray intensities for dead-time and background, so that the scaler readings can be directly used as input. As to the simplifications contained in MULTI8, and also used in FRAME, we have concluded that they will not observably degrade the accuracy of the procedure if certain working conditions are adopted. The working rules concerning the choice of lines and operating voltage are discussed at the end of the paper. A comparison of important features of the three programs mentioned above is found in Table I.

## Fundamentals of FRAME (See Figure 1)

We have adapted from MULTI8, essentially without change, the multiplicative correction factors for absorption of primary radiation, of the atomic number effects, and of fluorescence due to characteristic lines (ZAF procedure). The program thus operates on the assumption that the relationship between concentration and background dead-time

corrected intensity ratios can be expressed by

$$C = k \cdot k_Z \cdot k_A \cdot k_F \qquad (1)$$

where C is the mass fraction of the element being measured

k is the x-ray intensity ratio obtained from the microprobe corrected for background and dead-time

$k_Z$ is the atomic number correction

$k_A$ is the absorption correction, and

$k_F$ is the characteristic fluorescence correction.

As in MULTI8, there is no provision for fluorescence due to the continuum. The significant changes with respect to MULTI8 are as follows.

1. As an input, FRAME can use x-ray photon counts collected in fixed time periods on scalers. A background correction is performed by subtracting background counts, which must also be accumulated in scalers, from the line intensities. The operator must determine from where the background readings are to be collected. In the present version, the background readings are made on the standards, and FRAME distinguishes background from standard line readings by the intensities of the observed radiation.

2. A correction for counter coincidence (dead-time), according to the equation of Ruark and Brammer [9] is applied to the observed count rates for specimens and standards. A method for determining the dead-time constant, $\tau$, has been described elsewhere [10]. The relative x-ray intensity ratio, k, is calculated for each measurement by dividing the corrected intensity from the specimen by that of the standard.

3. The energies of the K, L, and M absorption edges are calculated by means of fits based on Moseley's law. The energies of the $K\alpha$, $L\alpha$, and $M\alpha$ lines are also calculated in the same way. One of these three lines is almost always chosen as the analytical line. If conditions unfavorable for analysis result from choice of line by the operator, a warning is printed by the program. The operator can then use another line or readjust the operating voltage, depending on the nature of the difficulty.

4. The correction for absorption in the specimen of primary x-rays is carried out with use of the absorption correction factor $f_p$ proposed by Heinrich and Yakowitz[2] [11]:

$$1/f_p = 1 + 3 \times 10^{-6} (E_o^{1.65} - E_q^{1.65})\chi + 4.5 \times 10^{-13} \cdot (E_o^{1.65} - E_q^{1.65})^2 \chi^2 \qquad (2)$$

where $\chi = \mu \csc \psi$; and $\psi$. is the x-ray emergence angle;

$E_o$ and $E_q$ are the operating voltage and critical excitation potential for the line of interest, in kilovolts.

The absorption correction is

$$k_A = f_p / f^*_p \qquad (3)$$

(Here, and in what follows, terms with an asterisk refer to the unknown, and terms without superscript refer to the standard.)

The mass attenuation coefficients are calculated as proposed by Heinrich [12]. To reduce requirements for storage, least squares fits were made to the logarithm of the coefficient C and the exponent n in the general relation:

[2] The exponent "-13" in the third term of equation (2) is correct. This value was erroneously given as "-14" in reference [11].

$$\mu = C\lambda^n$$

in which $\lambda$ is the wavelength in angstroms.

A comparison of the calculated values with those given by Heinrich [12] showed agreement within a few percent. To avoid uncertainties which arise where lines close to edges are used, a warning is printed if the analytical line falls within 100 eV of an absorption edge of another element present in the specimen.

5. The correction for atomic number used in FRAME is:

$$k_Z = \left(\frac{R^*}{R}\right)\left(\frac{\overline{S}}{\overline{S}^*}\right) \qquad (4)$$

The electron backscattering correction factors, R and R*, are those obtained by Duncumb and Reed from Monte Carlo calculations [13], fitted by us with respect to the overvoltage, U, and the mean atomic number, $\overline{Z}$, as follows:

$$R = R_1 - R_2 \ln (R_3\overline{Z} + 25) \qquad (5)$$

where $R_1 = 8.73 \times 10^{-3}U^3 - 0.1669U^2 + 0.9662U - 0.4523$

$R_2 = 2.703 \times 10^{-3}U^3 - 5.182 \times 10^{-2}U^2 + 0.302U - 0.1836$

$R_3 = (0.887U^3 - 3.44U^2 + 9.33U - 6.43)/U^3$

$U = E_o/E_q$, $\overline{Z} = \Sigma\, C_i Z_i$, $C_i$ = weight fraction of element i.

If U > 10, then U is set equal to 10.

Figure 2 shows the values given by Duncumb and Reed and the curves predicted by equation (5). The value of R* is obtained from $R^* = \sum_{k_i=1}^{n} C_i R_i$. (6)

Equation (5) is simpler than the fifth-order fit in voltage and atomic number [14] used in MULTI8 and COR2, and gives very similar results.

The term $\overline{S}$ in equation (4) is an average stopping power according to a form of Bethe's equation [15]. The stopping power calculation is identical to that in MULTI8, except that the mean electron energy is obtained, as previously proposed by Thomas [16], as follows:

$$\overline{E} = \frac{E_o - E_q}{2}.$$

This approximation is sufficiently accurate except at extreme overvoltage values which should be avoided for accurate analysis [17]. The atomic weights, required for the stopping power calculation, are stored in the program.

As in MULTI8, the characteristic fluorescence correction is performed with the aid of Reed's equation [18]. MULTI8 and COR2 require the input of fluorescent yields; in COR2 these are stored in the permanent data file. In FRAME we use the fluorescence yields for K and L shells which are calculated by means of empirical fits. No fluorescence correction is carried out if fluorescence is excited by M lines. We assume that the absorption jump ratio is 0.88 for the K edge and 0.75 for the $L_3$ edge.

FRAME contains the following provisions which decide whether fluorescence correction is required. Call $E_\ell$ the energy of the exciting line (K- or L-line), $E_K$ and $E_L$ the critical excitation potentials for the excited K- and L-lines.

If $0 < (E_\ell - E_K) \leq 5$ then the K-line is indirectly excited.

If $0 < (E_\ell - E_L) \leq 3.5$, then the L-line is indirectly excited.

If fluorescent excitation occurs, the program prints a message to this effect. Then, it calculates the new mass attenuation coefficients required for Reed's equation [18] and performs the necessary calculation for the fluorescence effect.

This automatic selection of corrections for fluorescent excitation where necessary eliminates the need for the operator to decide if such corrections must be applied.

As mentioned previously [2], the iteration procedure used in MULTI8 and COR2 — and again in FRAME — converges very rapidly. For this reason, we stop the iteration after three cycles in order to reduce the time of computation. The resulting errors are smaller than the errors of measurement.

## Structure of the Program Versions FRAME2 to FRAME4

The version of FRAME which is reproduced in Appendix I is called FRAME3. The list of symbols used in FRAME3 is in Appendix II. This version is adapted for on-line processing of microprobe data on an EMR-6135[3] computer. FRAME2 is a computationally identical version for batch-processing on UNIVAC 1108; FRAME4 is adapted to a telephone-transmittal time-share system. The statement lists of FRAME2 and FRAME4 are available on request. The sectors for input and output will require modifications for use on other computers. These adaptations should be easy to carry out. Areas of the program specific to our set-up are identified by comment statements in the appended program list.

FRAME3 can be considered a model for on-line application. The first part (2.8K) of this version (with subroutines CFCAL and MAC) performs all preliminary calculations which are

[3] Identification of any specific instrument does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

independent of the composition of the specimen and standard, and do not, therefore, require x-ray intensity data. The second part (with subroutine QUDAT, 1.5K) uses the measured x-ray intensities from standards and unknowns to compute intensity ratios, which then are converted to concentrations, by means of the correction factors obtained in CFCAL. For a particular case — which may extend over several points to be analyzed — the first part is calculated only once, while the second part is executed every time a measurement is being performed. The interaction of the main program with the subprograms can be observed on the flow-diagram in Figure 1.

Limitations of FRAME

As mentioned above, the limitations of available memory have required several simplifications, (e.g., omission of the correction for fluorescence due to the continuum). These simplifications will not cause significant increase in the error of the analyses, as long as the following operational conditions are maintained:

1. The overvoltage ($E_o/E_q$) should not be smaller than 1.5.
2. The primary x-ray absorption factor, $f_p$, should not be smaller than 0.75.
3. If an x-ray line falls within 100 eV on the high energy side of an absorption edge, or 30 eV on the low energy side of any element present, then this line should not be used because of the uncertainties concerning mass absorption coefficients near the edge.

The restrictions imposed by these conditions are not serious or specific to FRAME, since working outside these specifications is unwise, even when a more detailed computer program is used. FRAME3 produces a printed warning when an analysis is computed with disregard of the above rules. In

the case of $f_p$, the warning criterion is applied to the absorption factor of the standard. For further control of conditions, the values of $f_p$ for the specimen are printed in the output of FRAME.

In our version of FRAME, it is assumed that the x-ray emergence angle is equal to 52.5°. The value of this angle can be changed by a single statement, and even a change to different angles for each spectrometer could be introduced without much effort.

The number of elements in the specimen is presently limited, in our versions, to six. Since the program is primarily intended for on-line use, it is assumed that the six intensities are read simultaneously. However, the number of x-ray lines which can be read simultaneously in an instrument cannot exceed that of the spectrometers, unless part of the information is provided by an energy-dispersive spectrometer. Since this limitation may be significant in the analysis of minerals, we consider introducing, in a later version, modifications which would permit the reading of x-ray intensities in two steps in time, so that spectrometers could be realigned to read more than one line per analysis.

We have also assumed that all measurements for a case were performed at the same operating voltage. If a two-step read-out is considered, this criterion will be modified so that, if desired, some lines can be read at a lower voltage than the rest. This experimental procedure is, however, awkard and is not used frequently. Therefore, the limitation to a single operating voltage is not stringent.

All versions of FRAME permit the determination of one element by difference. The use of stoichiometric relations to determine the concentration of one element is provided in FRAME4 and can easily be incorporated into other versions.

At present, it is not possible to replace the mass absorption coefficients calculated in the program by others provided externally. Such a feature will be incorporated later, as well as an option to assume that the concentration of certain elements is known. We also plan to indicate at a later date, modifications to obtain atomic fractions rather than weight fractions. The number of iterations, which presently is limited to three, could be changed by a simple statement. However, as indicated by the data presented in Tables II and III, computation beyond three iterations does not provide any significant improvement in accuracy.

## Comparison of Results from FRAME with COR2

We have compared the FRAME and COR correction programs, using the measurements on 228 binary alloys listed by Poole [19], as well as 16 analyses on the binary alloys Au-Ag and Au-Cu designated NBS Standard Reference Materials 481 and 482, respectively, [20]. The analyses listed by Poole were performed in several laboratories from all over the world, and they cover a variety of systems and experimental conditions.

A comparison of the results by FRAME with those by COR2 for the Poole-Thomas compilation is shown in Figure 3. We note that the disagreement between COR2 and FRAME is small compared with the errors shown in the diagram for COR2. We also note that larger discrepancies occur when the operating conditions are outside the suggested boundaries.

Analyses performed at NBS are presented in Tables II, III, and IV. The results show that FRAME is suitable for a wide variety of analytical studies. They also show, in the case of the two minerals analyzed, that the method of determining the background level was not critically important.

An example of the input and output for the analysis of the Diopside 65 - Jadeite 35 is shown in Table V. All required input statements follow a colon or question mark. The program

version is FRAME4. Table V shows that the concentrations obtained by calculating oxygen by difference or by stoichiometric relations are the same. The FRAME4 routine was run on a time-shared computer with background dead-time corrected relative intensity ratios (k-values) already calculated. The k-values shown are referred to pure element standards as calculated from the mineral standards listed in Table IV.

## Example Showing On-line Analysis using FRAME

An iron-silicon alloy containing 3.22% Si and 96.8% Fe, designated SRM-483, was analyzed. This material is certified to be homogeneous with respect to iron and silicon [21]. Five individual analyses were carried out. The results, as printed on a teletype display during analysis, are shown in Table VI. The average silicon content is 3.34%, and the average iron content is 96.2%.

## Conclusions

The FRAME program is entirely suitable for on-line or off-line use to reduce data from the electron probe microanalyzer to concentrations of the elements present. FRAME employs the analytical ZAF approach, but only occupies about 4K of computer memory. The FRAME program should be readily adaptable to most mini-computers for use in many microprobe laboratories.

Comparisons have shown that FRAME give virtually the same results as the much larger batch-type program, COR, provided that fluorescence effects due to the continuum can be safely neglected. All of the data discussed in this paper, including those reported by Poole, fall into this category. The input requirements for FRAME are virtually the same,

however (see Table I). Results on two minerals, Johnstown Hypersthene and Diopside 65 - Jadeite 35, give results close to the chemical analysis (Tables III, IV and V). Furthermore, the results were only slightly affected by the method of determining background level or by using FRAME to calculate the results obtaining the oxygen content by difference or by stoichiometric relations.

Table Ia. Comparison of NBS programs for quantitative microprobe analysis

| | COR2 | MULTI8 | FRAME3 |
|---|---|---|---|
| | MECHANICAL ASPECTS | | |
| Memory | 50 K | 4 K | 4 K |
| Intended mode of operation | Batch | Time-share | Time-share or dedicated |
| Input | Cards and magnetic tape | Teletype | Teletype or on-line |
| Output | Line printer | Teletype | Teletype |

Table Ib. Comparison of NBS programs for quantitative microprobe analysis

| | COR2 | MULTI8 | FRAME3 |
|---|---|---|---|
| | INPUT | | |
| No. of elements | Yes | Yes | Yes |
| Atomic numbers | Yes | Yes | Yes |
| Atomic weights | Data file | Yes | Stored |
| Operating voltage | Yes | Yes | Yes |
| Line | Yes | No | Yes |
| Crit. excit. potential | Data file | Yes | Calculated |
| Fluorescence yield | Data file | Yes | Calculated |
| $\mu/\rho$ | Calculated | Yes | Calculated |
| Fluorescence-decisions | Made internally | Yes | Made internally |
| Valences | Yes (if used) | Yes (if used) | Yes (if used) |
| X-ray intensities | Raw or k-values | k-values only | Raw or k-values |

Table Ic. Comparison of NBS programs for quantitative microprobe analysis

| | COR2 | MULTI8 | FRAME3 |
|---|---|---|---|
| | CONTENTS and OPTIONS | | |
| Background | Yes | No | Yes |
| Dead-time | Yes | No | Yes |
| Atomic-number correction | Philibert-Tixier | Thomas modified | Thomas modified |
| Absorption correction | Philibert-Duncumb Heinrich sigma | Philibert-Duncumb Heinrich sigma | Heinrich-Yakowitz |
| Characteristic fluorescence | Hénoc | Reed | Reed |
| Continuum fluorescence | Hénoc | No | No |
| k-values | Yes | Yes | Yes |
| Element by difference | Yes | Yes | Yes |
| Element by stoichiometry | Yes | Yes | Yes |
| Element with fixed conc. | Yes | No | Not yet |

Table II. Analysis of alloys: SRM's 481 and 482 (Au-Ag and Cu-Au)

| Element and line | Operating voltage (kv) | $k_{meas.}$ | $C_{FRAME}$ Itr.*I | $C_{FRAME}$ Itr.*II | $C_{FRAME}$ Itr.*III final | $C_{COR2}$ | C Certified | f(χ) |
|---|---|---|---|---|---|---|---|---|
| Au-Mα | 10 | 0.201 | 0.227 | 0.227 | 0.227 | 0.234 | 0.2243 | 0.84 |
| Au-Mα | 10 | 0.362 | 0.399 | 0.399 | 0.399 | 0.409 | 0.4003 | 0.84 |
| Au-Mα | 10 | 0.559 | 0.598 | 0.598 | 0.598 | 0.608 | 0.6005 | 0.84 |
| Au-Mα | 10 | 0.771 | 0.799 | 0.799 | 0.799 | 0.806 | 0.8005 | 0.85 |
| Ag-Lα | 10 | 0.764 | 0.778 | 0.776 | 0.776 | 0.764 | 0.7758 | 0.89 |
| Ag-Lα | 10 | 0.584 | 0.600 | 0.598 | 0.598 | 0.582 | 0.5993 | 0.86 |
| Ag-Lα | 10 | 0.386 | 0.399 | 0.398 | 0.398 | 0.382 | 0.3992 | 0.83 |
| Ag-Lα | 10 | 0.191 | 0.198 | 0.197 | 0.197 | 0.187 | 0.1996 | 0.80 |
| Cu-Kα | 25 | 0.240 | 0.206 | 0.205 | 0.205 | 0.203 | 0.1983 | 0.90 |
| Cu-Kα | 25 | 0.453 | 0.413 | 0.411 | 0.411 | 0.402 | 0.3964 | 0.91 |
| Cu-Kα | 25 | 0.651 | 0.619 | 0.618 | 0.617 | 0.604 | 0.5992 | 0.93 |
| Cu-Kα | 25 | 0.834 | 0.818 | 0.817 | 0.817 | 0.805 | 0.7985 | 0.95 |
| Au-Lα | 25 | 0.745 | 0.788 | 0.795 | 0.795 | 0.794 | 0.8015 | 0.92 |
| Au-Lα | 25 | 0.529 | 0.592 | 0.598 | 0.598 | 0.598 | 0.6036 | 0.91 |
| Au-Lα | 25 | 0.331 | 0.391 | 0.395 | 0.395 | 0.396 | 0.4010 | 0.90 |
| Au-Lα | 25 | 0.154 | 0.192 | 0.193 | 0.193 | 0.194 | 0.2012 | 0.89 |

*Itr. is the abbreviation for iteration.

Table III. Analysis of a silicate: Diopside 65 - Jadeite 35
(done with oxygen by stoichiometry using FRAME4)

10 kV = $E_o$

| | Na | Mg | Al | Si | Ca |
|---|---|---|---|---|---|
| $k_m$* | 0.0281 | 0.0593 | 0.0363 | 0.236 | 0.111 |
| C† - Iteration I | 0.0392 | 0.0730 | 0.0439 | 0.270 | 0.121 |
| C - Iteration II | 0.0384 | 0.0718 | 0.0433 | 0.268 | 0.121 |
| C - Iteration III | 0.0384 | 0.0718 | 0.0433 | 0.268 | 0.121 |
| C - Chemical Analysis | 0.0398 | 0.073 | 0.0467 | 0.266 | 0.120 |
| $f_p$ | 0.69 | 0.77 | 0.81 | 0.86 | 0.97 |

*$k_m$ - measured intensity ratio corrected for background and dead-time effects.

†C - mass fraction

Table IV. Analysis of the silicates: Johnstown Hypersthene and Diopside 65 - Jadeite 35, using FRAME4

Chemical analysis of minerals used

| Mineral | Na | Mg | Al | Si | Ca | Ti | Fe |
|---|---|---|---|---|---|---|---|
| NaCl | 0.393 | | | | | | |
| $SiO_2$ | | | | 0.467 | | | |
| Fayalite | -- | -- | -- | 0.137 | -- | -- | 0.525 |
| Diopside·2%$TiO_2$ | -- | 0.110 | -- | 0.254 | 0.181 | 0.012 | -- |
| Garnet 110752 | -- | 0.043 | 0.120 | 0.188 | $0.129_5$ | 0.002 | 0.088 |
| Diopside 65 - Jadeite 35 | 0.0398 | 0.073 | 0.0467 | 0.266 | 0.120 | -- | -- |
| Johnstown Hypersthene | -- | 0.164 | 0.002 | 0.251 | 0.0099 | 0.0013 | 0.121 |

Standards used:

NaCl for Na in diopside 65 - Jadeite 35
$SiO_2$ for Si in both
Fayalite for Fe in Johnstown Hypersthene
Diopside·2%$TiO_2$ for Mg, Ca, Ti, in Johnstown Hypersthene
Garnet 110752 for Mg, Al, Ca, in Diopside 65 - Jadeite 35

$Al_2O_3$ used as BKG specimen for Fe, Si, Mg, Ca, Ti
MgO used as BKG specimen for Na, Al, Ca
} Scheme I

Off-peak (above and below used for all elements Scheme II

Table IV. Continued

Analysis of Johnstown Hypersthene**

$E_o$ = 15 kV

| | Mg | Si | Ca | Ti | Fe |
|---|---|---|---|---|---|
| $k_m^*$ - S1 | 0.114 | 0.202 | 0.011 | 0.0008 | 0.104 |
| $k_m^*$ - S2 | 0.117 | 0.202 | 0.010 | 0.0007 | 0.104 |
| $C^\dagger_{CALC}$ - S1 | 0.165 | 0.260 | 0.0110 | 0.0009 | 0.121 |
| $C^\dagger_{CALC}$ - S2 | 0.169 | 0.260 | 0.0110 | 0.0008 | 0.121 |
| C - Chemical Analysis | 0.164 | 0.251 | 0.0099 | 0.0013 | 0.121 |

Analysis of Diopside 65 - Jadeite 35

$E_o$ = 10 kV

| | Na | Mg | Al | Si | Ca |
|---|---|---|---|---|---|
| $k_m^*$ - S1 | 0.0281 | 0.0593 | 0.0363 | 0.236 | 0.111 |
| $k_m^*$ - S2 | 0.0275 | 0.0595 | 0.0363 | 0.236 | 0.111 |
| $C^\dagger_{CALC}$ - S1 | 0.0384 | 0.0716 | 0.0433 | 0.268 | 0.121 |
| $C^\dagger_{CALC}$ - S2 | 0.0375 | 0.0718 | 0.0433 | 0.268 | 0.121 |
| C - Chemical Analysis | 0.0398 | 0.073 | 0.0467 | 0.266 | 0.120 |

**Analysis carried out calculating oxygen by stoichiometry was exactly the same as that carried out calculating oxygen by difference.

S1 - Background taken on $Al_2O_3$ or MgO

S2 - Background taken off-peak

$k_m^*$ - Measured intensity ratio corrected for background and dead-time effects.

$C^\dagger$ - Mass fraction

Table V. Input-output for FRAME4 —
analysis of Diopside 65 - Jadeite 35

(a) Analysis with oxygen calculated by difference.

```
NUMBER OF ELEMENTS AND EO: 6 10
ATOMIC NUMBER AND LINE FOR EACH: 11 1 12 1 13 1 14 1 20 1 8 0
WARNING - THE LINE OF    11    IS CLOSE TO AN EDGE OF     11
ELEMENT       11     IS EXCITED BY ELEMENT       12
ELEMENT       11     IS EXCITED BY ELEMENT       13
ELEMENT       11     IS EXCITED BY ELEMENT       14
ELEMENT       11     IS EXCITED BY ELEMENT       20
ELEMENT       12     IS EXCITED BY ELEMENT       13
ELEMENT       12     IS EXCITED BY ELEMENT       14
ELEMENT       12     IS EXCITED BY ELEMENT       20
ELEMENT       13     IS EXCITED BY ELEMENT       14
ELEMENT       13     IS EXCITED BY ELEMENT       20
ELEMENT       14     IS EXCITED BY ELEMENT       20
VALENCES:0 0 0 0 0 0
STANDARDS DATA? NO
K-VALUES: .0281 .0593 .0363 .2364 .111
AT. NO.      K-VALUE      CONCENTRATION      F(X)

 11.          .0281           .0384          .6867
 12.          .0593           .0718          .7690
 13.          .0363           .0433          .8121
 14.          .2364           .2685          .8555
 20.          .1110           .1207          .9670
  8.         0.0000           .4573         1.0000
TOTAL C =1.0000
```

(b) Analysis with oxygen calculated stoichiometrically.

```
NUMBER OF ELEMENTS AND EO: 6 10
ATOMIC NUMBER AND LINE FOR EACH: 11 1 12 1 13 1 14 1 20 1 8 0
WARNING - THE LINE OF    11    IS CLOSE TO AN EDGE OF     11
ELEMENT       11     IS EXCITED BY ELEMENT       12
ELEMENT       11     IS EXCITED BY ELEMENT       13
ELEMENT       11     IS EXCITED BY ELEMENT       14
ELEMENT       11     IS EXCITED BY ELEMENT       20
ELEMENT       12     IS EXCITED BY ELEMENT       13
ELEMENT       12     IS EXCITED BY ELEMENT       14
ELEMENT       12     IS EXCITED BY ELEMENT       20
ELEMENT       13     IS EXCITED BY ELEMENT       14
ELEMENT       13     IS EXCITED BY ELEMENT       20
ELEMENT       14     IS EXCITED BY ELEMENT       20
VALENCES:1 2 3 4 2 2
STANDARDS DATA? NO
K-VALUES: .0281 .0593 .0363 .2364 .111
AT. NO.      K-VALUE      CONCENTRATION      F(X)

 11.          .0281           .0384          .6871
 12.          .0593           .0718          .7693
 13.          .0363           .0433          .8123
 14.          .2364           .2685          .8557
 20.          .1110           .1207          .9671
  8.         0.0000           .4531         1.0000
TOTAL C = .9957
```

Table VI. Results of analysis of SRM 483 containing 0.0322 Si - 0.968 Fe. Analysis performed "on-line" at NBS

FRAME3 1118HRS 187 DAY, 1973

ELECTRON PROBE ANALYSIS 15.0 KV

ELEMENT 14 IS EXCITED BY ELEMENT 26

| Z-LINE | Z-ABSORBER | MASS ABS. COEFF. |
|---|---|---|
| 14 | 14 | 330.0 |
| 14 | 26 | 2495.8 |
| 26 | 14 | 113.8 |
| 26 | 26 | 70.9 |

| AT. NO. | K-VALUE | CONC | F(CHI) |
|---|---|---|---|
| 14 | .0237 | .0337 | .5544 |
| 26 | .9532 | .9595 | .9834 |
| | TOTAL C = | .9932 | |
| 14 | .0233 | .0332 | .5543 |
| 26 | .9583 | .9640 | .9834 |
| | TOTAL C = | .9972 | |
| 14 | .0238 | .0339 | .5544 |
| 26 | .9530 | .9593 | .9834 |
| | TOTAL C = | .9932 | |
| 14 | .0234 | .0333 | .5543 |
| 26 | .9573 | .9635 | .9834 |
| | TOTAL C = | .9968 | |
| 14 | .0236 | .0337 | .5544 |
| 26 | .9552 | .9612 | .9834 |
| | TOTAL C = | .9949 | |

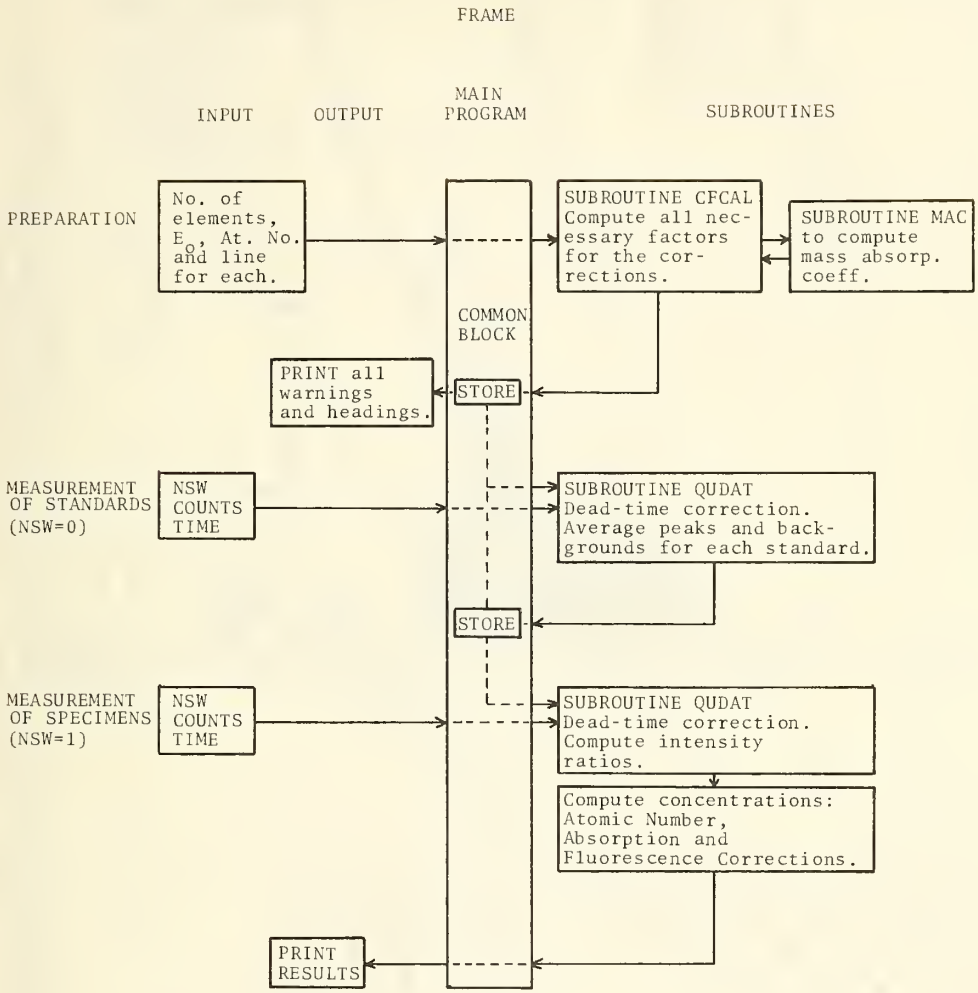
FRAME
INPUT
OUTPUT
MAIN PROGRAM
SUBROUTINES
PREPARATION
No. of elements, $E_o$, At. No. and line for each.
SUBROUTINE CFCAL Compute all necessary factors for the corrections.
SUBROUTINE MAC to compute mass absorp. coeff.
COMMON BLOCK
PRINT all warnings and headings.
STORE
MEASUREMENT OF STANDARDS (NSW=0)
NSW COUNTS TIME
SUBROUTINE QUDAT Dead-time correction. Average peaks and backgrounds for each standard.
STORE
MEASUREMENT OF SPECIMENS (NSW=1)
NSW COUNTS TIME
SUBROUTINE QUDAT Dead-time correction. Compute intensity ratios.
Compute concentrations: Atomic Number, Absorption and Fluorescence Corrections.
PRINT RESULTS

Figure 1. Flow sheet showing operations carried out by FRAME program.

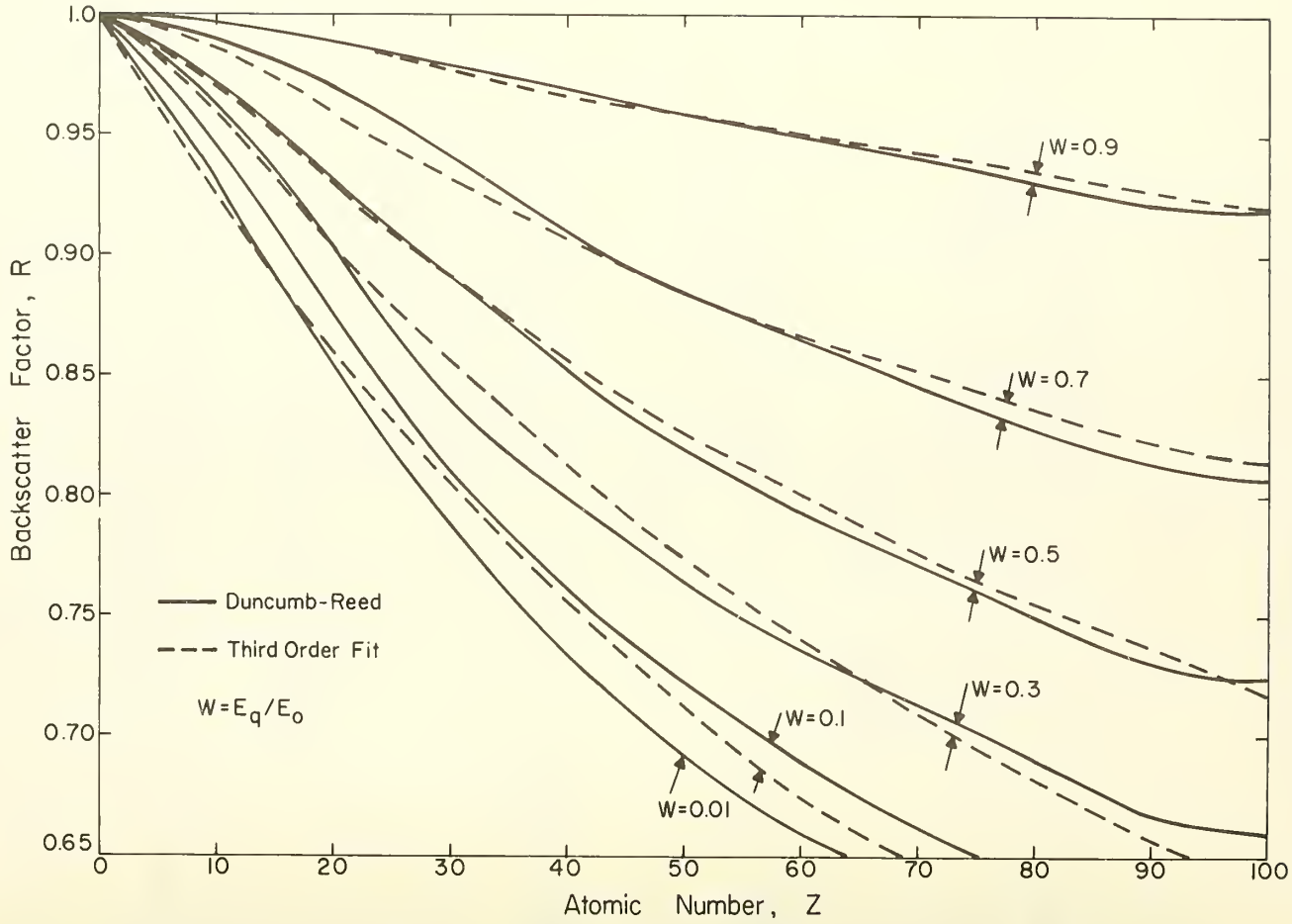


Figure 2. Analytical fit to backscatter factor R. Solid lines given by Duncumb and Reed [5]; dottled lines fitted by equation 5. For $W \leq 0.1$ the FRAME program uses R corresponding to W=0.1.

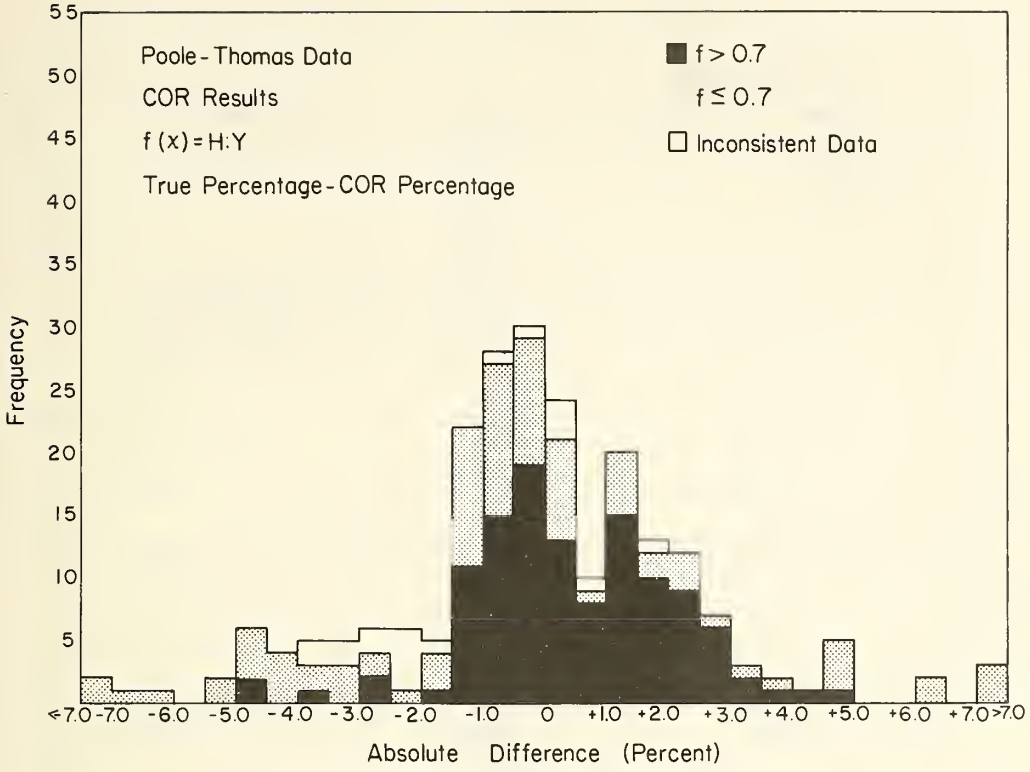


Figure 3a. Results of analysis on alloy data quoted by Poole [19] as computed by COR using the Heinrich-Yakowitz $f(\chi)$ expression [11].

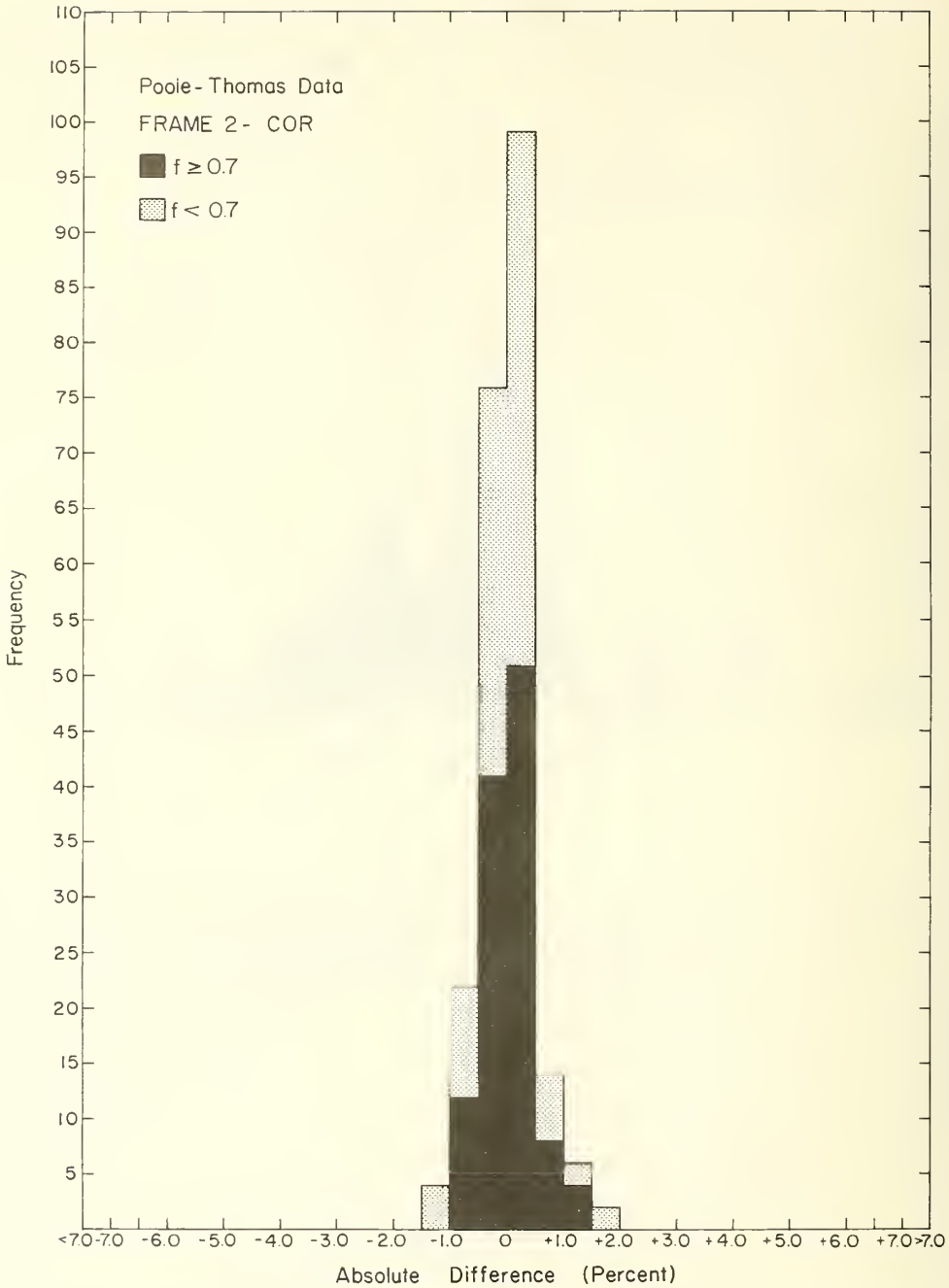


Figure 3b. Comparison of FRAME2 and COR for the alloy data shown by Figure 3a.

## References


[1] Heinrich, K. F. J., Editor, "Quantitative Electron Probe Microanalysis," NBS Special Publication 298, U.S. Government Printing Office, Washington, D. C. (1968).

[2] Heinrich, K. F. J., Anal. Chem. 44, 350 (1972).

[3] Hénoc, J., Heinrich, K. F. J., and Myklebust, R. L., "A Rigorous Correction Procedure for Quantitative Electron Probe Microanalysis (COR 2)," U.S. Natl. Bur. Stds. Technical Note 769, U.S. Government Printing Office, Washington, D. C. (1973).

[4] Ziebold, T. O. and Ogilvie, R. E., Anal. Chem. 36, 322 (1964).

[5] Bence, A. E. and Albee, A. L., J. Geology 76, 382 (1968).

[6] Chodos, A. A. and Albee, A. L., Proc. Sixth Natl. Conf. on Electron Probe Analysis, Pittsburgh, Pa., p. 15A (1971).

[7] Philibert, J. and Tixier, R. in "Quantitative Electron Probe Microanalysis," Heinrich, K. F. J., Editor, NBS Special Publication 298, p. 13, U.S. Government Printing Office, Washington, D. C. (1968).

[8] Heinrich, K. F. J., Myklebust, R. L., Yakowitz, H., and Rasberry, S. D., "A Simple Correction Procedure for Quantitative Electron Probe Microanalysis," U.S. Natl. Bur. Stds. Technical Note 719, U.S. Government Printing Office, Washington, D. C. (1972).

[9] Ruark, A. and Brammer, F. E., Phys. Rev. 52, 322 (1937).

[10] Heinrich, K. F. J., Vieth, D. L., and Yakowitz, H., in Advances in X-Ray Analysis, Vol. 9, Mallett, G. R., Fay, M. J., and Mueller, W. M., Editors, p. 208, Plenum Press, New York (1966).

[11] Heinrich, K. F. J., Yakowitz, H., and Vieth, D. L., Proc. Seventh Natl. Conf. on Electron Probe Microanalysis, San Francisco, CA, paper no. 3, 6 pp. (1972).

[12] Heinrich, K. F. J., in The Electron Microprobe, McKinley, T. D., Heinrich, K. F. J., and Wittry, D. B., Editors, p. 296, John Wiley & Sons, Inc., New York (1966).

[13] Duncumb, P. and Reed, S. J. B., in "Quantitative Electron Probe Microanalysis," Heinrich, K. F. J., Editor, NBS Special Publication 298, p. 133, U.S. Government Printing Office, Washington, D. C. (1968).

[14] Heinrich, K. F. J., in "Present State of the Classical Theory of Quantitative Electron Probe Microanalysis," NBS Technical Note 521, p. 5, U.S. Government Printing Office, Washington, D. C. (1970).

[15] Heinrich, K. F. J., Anal. Chem. 44, 350 (1972).

[16] Thomas, P. M., AERE Report 4593, U. K. Atomic Energy Authority (1964). Also see reference [12].

[17] Heinrich, K. F. J. and Yakowitz, H., Mikrochim. Acta 1970, p. 123.

[18] Reed, S. J. B., Brit. J. Appl. Phys. 16, 913 (1965).

[19] Poole, D. M., in "Quantitative Electron Probe Microanalysis," Heinrich, K. F. J., Editor, NBS Special Publication 298, p. 93, U.S. Government Printing Office, Washington, D. C. (1968).

[20] Heinrich, K. F. J., Myklebust, R. L., and Rasberry, S. D., "Preparation and Evaluation of SRM's 481 and 482 Gold-Silver and Gold-Copper Alloys for Microanalysis," NBS Special Publication 260-28, U.S. Government Printing Office, Washington, D. C. (1971).

[21] Yakowitz, H., Fiori, C. E., and Michaelis, R. E., "Homogeneity Characterization of Fe-3Si Alloy," NBS Special Publication 260-22, U. S. Government Printing Office, Washington, D. C. (1971).

# APPENDIX I

## Listing of FRAME3 in FORTRAN IV

```
C                              FRAME3

C  ON-LINE PROGRAM FOR QUANTITATIVE ELECTRON PROBE MICROANALYSIS.
C                FORTRAN IV      MAY 22, 1973
C  THE INPUT AND OUTPUT WILL NEED TO BE MODIFIED TO FIT THE COMPUTER
C  BEING USED.
C  NOTE - ALL STATEMENTS PRECEDED BY AN * RESULT FROM SYSTEM ROUTINES
C  ON THE ANALYTICAL CHEMISTRY DIVISIONS COMPUTER FOR DATA ACQUISITION
C  AND CONTROL.


      SUBROUTINE CFCAL(TAB)

C  THIS ROUTINE IS LOADED FIRST TOGETHER WITH MAC.  READ THE INITIAL
C  INPUT PARAMETERS AND COMPUTE ALL NECESSARY CONSTANTS.

      INTEGER MESS(40),PST
*     INTEGER TAB,CRLF
      REAL JI
*     LOGICAL SETSW
      DIMENSION Z(6),EC(9,6),EL(3,6),LI(6),EQ(6),E(6),AC(6,6),FAC(6,6),H
     1(6),FC(6),R(6,6),S(6,6),U(6),KEY(6,6),C1(9),C2(9),C3(9)
     2 ,P(6),R1(6),OM(6),A(6),X(6),AN(92),Y(6)
*     DIMENSION ISPC(4),IFDB(3)
      DIMENSION MHD(5),IZ(6)
      DIMENSION XL(6),XXK(6),BK(6),PK(6),PB(6)
      DIMENSION IBUF(50),SC(7)
      COMMON/ENER/EL,EC
      COMMON/STORE/N,N1,LI,S,R,AC,H,KEY,FAC,EO,EQ,P,OM,R1,X,Y,A,FC,Z,SC,
     1SETSW,IBUF,PST,NFSW,NFLAG,XL,XXK,BK,PK,PB,COSEC
*     COMMON/ESTOR/IDUM
      EQUIVALENCE(MESS(1),CRLF)
      DATA AN/1.008,4.003,6.94,9.013,10.82,12.011,14.007,16.,19.,20.18,
     122.99,24.31,26.98,28.09,30.97,32.06,35.45,39.95,39.1,40.08,44.96,
     247.9,50.94,52.,54.94,55.85,58.93,58.71,63.54,65.37,69.72,72.59,
     374.92,78.96,79.91,83.8,85.47,87.62,88.91,91.22,92.91,95.94,99.,
     4101H1,102.9,106.4,107.9,112.4,114.8,118.7,121.8,127.6,126.9,131.3,
     5132H9,137.3,138.9,140.1,140.9,144.2,145.,150.4,152.,157.2,158.9,
     6162.5,164.9,167.3,168.9,173.,175.,178.5,180.95,183.85,186.2,190.2,
     7192.2,195.1,196.97,200.6,204.4,207.2,209.,210.,210.,222.,223.,226.
     8,227.,232.,231.,238./
      DATA C1/-.0397931,-.0339160,-.0865397,-.2283427,1.251788,
     1.8349031,.4422173,.2514096,.2729506/
      DATA C2/2.423000,2.825262,3.323153,4.311724,-7.837999,
     1-4.149247,-.9792409,.9319132,.6889060/
      DATA C3/5.509104,9.035256,10.25054,12.00253,-11.58026,
     1-3.338016,3.153478,8.035612,7.424300/

C  THE FOLLOWING CONSTANTS ARE NEEDED BY OUR COMPUTER TO PRINT OUT THE
C  RESULTS ON A TELETYPE.

*     DATA ISPC/2*$41503,2*$41101/
*     DATA IADTTY/$176145/
*     DATA IFDB(2)/0/
*     DATA IPRI/10/
*     DATA CRLF/$41101/

C  THE FOLLOWING STATEMENTS APPLY TO OUR COMPUTER AND ARE EQUIVALENT TO
C  READING THE INPUT DATA.
C  THIS SECTION READS AND DECODES A BUFFER CONTAINING THE INPUT
C  PARAMETERS - EO(KILOVOLTS), LI(LINE- 1=K, 2=L, 3=M, 0= NOT ANALYZED),
C  N(NUMBER OF ELEMENTS), IZ(ATOMIC NUMBER).
```

```
*     CALL RESTOR(TAB)
*     I = KBCDBN(IEXTR(5,16,IBUF(8)))
      EO=I/10.
*     LI(1) = IEXTR(13,16,IBUF(12))
*     LI(2) = IEXTR(10,12,IBUF(12))
*     LI(3) = IEXTR(7,9,IBUF(12))
*     LI(4) = IEXTR(4,6,IBUF(12))
*     LI(5) = IEXTR(1,3,IBUF(12))
*     LI(6) = IEXTR(13,16,IBUF(11))
*     N = IEXTR(1,4,IBUF(11))
*     IZ(1)= KBCDBN(IEXTR(9,16,IBUF(14)))
*     IZ(2)= KBCDBN(IEXTR(1,8,IBUF(14)))
*     IZ(3)= KBCDBN(IEXTR(9,16,IBUF(13)))
*     IZ(4)= KBCDBN(IEXTR(1,8,IBUF(13)))
*     IZ(5)= KBCDBN(IEXTR(9,16,IBUF(16)))
*     IZ(6)= KBCDBN(IEXTR(1,8,IBUF(16)))
      DO 10 I=1,6
   10 Z(I)=FLOAT(IZ(I))
      COSEC=1.2605
      N1=N
      IF(LI(N).EQ.0) N1=N-1

C  OPEN THE BUFFERS FOR STORING TELETYPE OUTPUT.

*     CALL ALU(LUTY,IADTTY)
*     CALL OPEN(LUTY,IFDB)
*     IF(IFDB(2).LE.0) CALL ERROR(721,TAB)
*     NW=4

C  RIOS IS THE SYSTEM I/O ROUTINE USED HERE FOR SPOOLING TELETYPE OUTPUT.
C  EVERYTHING IS PRINTED ON THE TELETYPE WHEN THIS FILE IS CLOSED
C  (STATEMENT 777). SCHENT IS THE SCHEDULED PROGRAM ENTRY FROM RIOS.
C  IS REPRESTNTS STATUS RETURNED FROM RIOS.

*     CALL RIOS2(0,0,IPRI,$1,LUTY,IADTTY,IS,NW,ISPC)
*    1 SCHENT
*     IF(IS.LE.0) GO TO 8

C  GET THE TIME OF YEAR.

*     CALL GDB(MHD)
      MHD(4)=MHD(4)+MHD(5)
      NYEAR=1973

C  PRINT TITLE AND DATE.

      ENCODE(72,2004,MESS(2),NC) MHD(4),MHD(3),NYEAR
 2004 FORMAT('   FRAME3    ',I4,'HRS  ',I3,' DAY, ',I4)
*     NW=18
*     CALL RIOS2(0,0,IPRI,$9,LUTY,IADTTY,IS,NW,MESS)
*    9 SCHENT
*     IF(IS.LE.0) GO TO 8
      MESS(2)=CRLF

C  PRINT KILOVOLTAGE.

      ENCODE(72,2001,MESS(3),NC) EO
 2001 FORMAT('ELECTRON PROBE ANALYSIS',1X,F4.1,' KV ')
      MESS(19)=CRLF
*     NW=19
*     CALL RIOS2(0,0,IPRI,$2,LUTY,IADTTY,IS,NW,MESS)
```

```
*    2 SCHENT
*      IF(IS.LE.0) GO TO 8

C   COMPUTE ALL ABSORPTION EDGES AND X-RAY LINES.

       DO 20 I=1,N
       ZL=ALOG(Z(I))
       DO 30 M=1,9
    30 EC(M,I)=EXP(C1(M)*ZL*ZL+C2(M)*ZL-C3(M))
       EL(1,I)=EXP(-.0188608*ZL*ZL+2.218585*ZL-5.170825)
       EL(2,I)=EXP(-.1239411*ZL*ZL+3.295325*ZL-9.758363)
       EL(3,I)=EXP(-.4755497*ZL*ZL+6.846618*ZL-20.08326)
       NZ=Z(I)
       A(I)=AN(NZ)
       L=LI(I)
       IF(L.EQ.0) GO TO 20
       LS=L*L
       EQ(I)=EC(LS,I)
       E(I)=EL(L,I)
       U(I)=EO/EQ(I)
       Y(I)=U(I)
       IF(U(I).GT.10.) U(I)=10.

C   PRINT WARNING IF THE OVERVOLTAGE IS LESS THAN 1.5.

       IF(U(I).GE.1.5) GO TO 20
       ENCODE(72,2006,MESS(2),NC) IZ(I)
  2006 FORMAT('WARNING - THE OVERVOLTAGE OF ELEMENT ',I2,' IS BELOW 1.5')
*      NW=27
*      CALL RIOS2(0,0,IPRI,$800,LUTY,IADTTY,IS,NW,MESS)
* 800 SCHENT
*      IF(IS.LE.0) GO TO 8
    20 CONTINUE
       DO 50 I=1,N1
       L=LI(I)
       DO 40 J=1,N

C   GET MASS ABSORPTION COEFFICIENTS.

       CALL MAC(I,L,J,Z,ABCO)
       DO 600 M=1,9
       IF(EC(M,J).LE.EL(L,I)-.1) GO TO 600
       IF(EC(M,J).GE.EL(L,I)+.03) GO TO 600

C   PRINT WARNING IF X-RAY LINE FALLS TOO NEAR AN ABSORPTION EDGE.

       ENCODE(72,2005,MESS(2),NC) IZ(I),IZ(J)
  2005 FORMAT('WARNING - THE LINE OF ',I2,' IS CLOSE TO AN EDGE OF ',I2)
*      NW=26
*      CALL RIOS2(0,0,IPRI,$900,LUTY,IADTTY,IS,NW,MESS)
* 900 SCHENT
*      IF(IS.LE.0) GO TO 8
       GO TO 40
   600 CONTINUE
    40 AC(J,I)=ABCO
    50 CONTINUE

C   COMPUTE BACKSCATTER COEFFICIENTS AND STOPPING POWERS.

       DO 200 I=1,N1
       A1=8.73E-3*U(I)**3-.1669*U(I)**2+.9662*U(I)+.4523
       B=2.703E-3*U(I)**3-5.182E-2*U(I)**2+.302*U(I)-.1836
```

```
      Q=.887-3.44/U(I)+9.33/U(I)**2-6.43/U(I)**3
      DO 100 J=1,N
      JI=9.76*Z(J)+58.5*Z(J)**(-.19)
      R(J,I)=A1-B*ALOG(Q*Z(J)+25.)
  100 S(J,I)=2.*Z(J)/(A(J)*(EO+EQ(I)))*ALOG(583.*(EO+EQ(I))/JI)

C  COMPUTE ABSORPTION CORRECTION.
C  PRINT WARNING IF CORRECTION IS TOO LARGE.

      H(I)=3.0E-6*(EO**1.65-EQ(I)**1.65)
      FC(I)=1.+H(I)*AC(I,I)*COSEC+H(I)**2*(AC(I,I)*COSEC)**2*.05
      RFC=1./FC(I)
      IF(RFC.GT.0.75) GO TO 3
      ENCODE(72,2002,MESS(2),NC) IZ(I),RFC
 2002 FORMAT('WARNING - THE F(X) OF ELEMENT ',I2,' IS',F5.3)
*     NW=21
*     CALL RIOS2(0,0,IPRI,$4,LUTY,IADTTY,IS,NW,MESS)
*   4 SCHENT
*     IF(IS.LE.0) GO TO 8
    3 CONTINUE

C  DETERMINE IF THERE IS A CHARACTERISTIC FLUORESCENCE CORRECTION.

      L=LI(I)
      GO TO (280,290,295),L
  280 CO=5.
      KK=0
      GO TO 340
  290 CO=3.5
      KK=1
      GO TO 340
  295 CO=3.5
      KK=2
  340 DO 300 J=1,N
      IF(J.EQ.I) GO TO 300
      K=1
  309 IF(EL(K,J)-EQ(I)) 330,330,310
  310 IF(EL(K,J)-EQ(I)-CO) 320,320,329
  320 KEY(I,J)=K+2*KK

C  PRINT THE FLUORESCENCE CORRECTIONS FOUND.

      ENCODE (72,2003,MESS(2),NC)IZ(I),IZ(J)
 2003 FORMAT( ' ELEMENT ',I2,' IS EXCITED BY ELEMENT ',I2)
*     NW=19
*     CALL RIOS2(0,0,IPRI,$5,LUTY,IADTTY,IS,NW,MESS)
*   5 SCHENT
*     IF(IS.LE.0) GO TO 8
      KS=K*K
      X(J)=EO/EC(KS,J)
      DO 325 M=1,N
      IF(EL(K,J)-E(M)) 325,335,325
  325 CONTINUE
      DO 11 II=1,N

C  GET ANY ADDITIONAL MASS ABSORPTION COEFFICIENTS REQUIRED.

      CALL MAC(J,K,II,Z,ABCO)
      FAC(II,J)=ABCO
   11 CONTINUE
      GO TO 330
  335 DO 336 II=1,N
```

```
  336 FAC(II,J)=AC(II,J)
      GO TO 330
  329 IF(K.EQ.2) GO TO 330
      K=2
      GO TO 309
  330 CONTINUE
  300 CONTINUE

C  SELECT PARAMETERS FOR CHARACTERISTIC FLUORESCENCE CORRECTION.

      DO 199 J=1,N
      IF(KEY(I,J).EQ.0) GO TO 199
      P(J)=1.
      R1(J)=.88
      K=KEY(I,J)
      GO TO (410,420,410,420,410,420),K
  410 OM(J)=EXP(2.373*ALOG(Z(J))-8.902)
      IF(K.EQ.1) GO TO 199
      IF(K.EQ.5) GO TO 198
      P(J)=.24
      R1(J)=.75
      GO TO 199
  420 OM(J)=EXP(2.946*ALOG(Z(J))-13.94)
      IF(K.EQ.6) GO TO 198
      IF(K.EQ.2) P(J)=4.2
      IF(K.EQ.4) R1(J)=.75
      GO TO 199
  198 P(J)=.02
      R1(J)=.5
  199 CONTINUE
  200 CONTINUE

C  PRINT TABLE OF MASS ABSORPTION COEFFICIENTS.

      ENCODE(72,708,MESS(2),NC)
  708 FORMAT('Z-LINE',5X,'Z-ABSORBER',5X,'MASS ABS. COEFF.')
*     NW=22
*     CALL RIOS2(0,0,IPRI,$12,LUTY,IADTTY,IS,NW,MESS)
*   12 SCHENT
*     IF(IS.LE.0) GO TO 8
*     NW=19
      DO 500 I=1,N1
      DO 400 J=1,N
      ENCODE(72,710,MESS(2),NC) IZ(I),IZ(J),AC(J,I)
  710 FORMAT(2X,I2,11X,I2,12X,F7.1)
*     CALL RIOS2(0,0,IPRI,$13,LUTY,IADTTY,IS,NW,MESS)
*   13 SCHENT
*     IF(IS.LE.0) GO TO 8
  400 CONTINUE
  500 CONTINUE
*     NW=1
*     CALL RIOS2(0,0,IPRI,$7,LUTY,IADTTY,IS,NW,CRLF)
*    7 SCHENT
*     IF(IS.LE.0) GO TO 8

C  PRINT HEADINGS.

      ENCODE(72,707,MESS(2),NC)
  707 FORMAT('AT. NO.',5X,'K-VALUE',5X,'CONC',8X,'F(CHI)')
*     NW=22
*     CALL RIOS2(0,0,IPRI,$6,LUTY,IADTTY,IS,NW,MESS)
*    6 SCHENT
```

```
C  CLOSE PRINT FILE.  THE FOLLOWING STATEMENTS APPLY TO OUR COMPUTER.

* 777 CALL CLOSE(LUTY,IFDB)
*      CALL  ERROR (333,TAB)
       NFSW=0

C  SAVE ALL PARAMETERS NEEDED IN QUDAT.

* 666 CALL SAVE(TAB)
       RETURN
8      CONTINUE
       END



       SUBROUTINE MAC(J,L,I,Z,ABCO)

C  LOAD WITH CFCAL.  THIS SUBROUTINE COMPUTES A MASS ABSORPTION
C  COEFFICIENT FOR ALL NECESSARY LINES AND ABSORBERS.

       DIMENSION EC(9,6),EL(3,6),Z(6), CN(4), D1(4),D2(4),D3(4),R(10)
       COMMON/ENER/EL,EC
       DATA D1/-.2322294,-.2544711,.2562163,1.359165/
       DATA D2/4.070053,4.769245,1.15119,-9.492116/
       DATA D3/-6.220746,-10.37878,-5.684848,18.64081/
       DATA R/1.,1.,1.17,1.63,1.,1.16,1.4,1.621,1.783,1./
       DATA CN(3),CN(4)/2.6,2.22/
       ZL=ALOG(Z(I))
       CN(1)=EXP(-.0045522*ZL*ZL-.0068535*ZL+1.070181)
       CN(2)=2.73
       IF(Z(I).LT.42.) GO TO 30
       CN(2)=EXP(-.1131595*ZL*ZL+.8368829*ZL-.5459687)
   30  CONTINUE
       DO 50 M=1,10
       IF(M.EQ.10) GO TO 40
       IF(EL(L,J).LT.EC(M,I)) GO TO 50
   40  MI=M-M/3-M/4-M/7
       C=EXP(D1(MI)*ZL*ZL+D2(MI)*ZL+D3(MI))/R(M)
       ABCO=C*(12.398/EL(L,J))**CN(MI)
       RETURN
   50  CONTINUE
       END



       SUBROUTINE QUDAT(NSW)

C  THIS SUBROUTINE TAKES DATA FROM THE SCALERS, COMPUTES AN INTENSITY
C  RATIO FOR EACH ELEMENT, AND THEN COMPUTES AND PRINTS THE
C  CONCENTRATIONS OF EACH ELEMENT.
C  THE OUTPUT IS PRINTED IN THE SAME MANNER AS IN CFCAL.

       REAL L,K
       INTEGER MESS(40),PST
*      INTEGER TAB,CRLF
*      LOGICAL SETSW
       DIMENSION Z(6),LI(6),EQ(6),AC(6,6),FAC(6,6),H(6),FC(6),R(6,6
      1),S(6,6),KEY(6,6),P(6),R1(6),OM(6),A(6),X(6),Y(6),XK(6),C(6),FCS(6
      2),W(6),XKF(6),BK(6),PK(6),PB(6),K(6),L(6),SF(6),ISPC(4),IFDB(3),SC
```

```
     3(7),IBUF(50)
      COMMON/STORE/N,N1,LI,S,R,AC,H,KEY,FAC,EO,EQ,P,OM,R1,X,Y,A,FC,Z,SC,
     1SETSW,IBUF,PST,NFSW,NFLAG,L,K,BK,PK,PB,COSEC
*     COMMON/ESTOR/IDUM
      EQUIVALENCE(MESS(1),CRLF)
*     DATA ISPC/2*$41503,2*$41101/
*     DATA IADTTY/$176145/
*     DATA IFDB(2)/0/
*     DATA IPRI/10/
*     DATA CRLF/$41101/
      DATA SF/6*1./
      DEADT(E)=E/(1.-E*3.E-6)

C  READ IN COMPOUND STANDARD FACTORS AT THIS POINT, OTHERWISE THEY ARE
C  ASSUMED EQUAL TO 1.    (SF(6))

      NI=N1+1
      IF(NFSW.EQ.1) GO TO 1

C  COLLECT AND STORE PEAK AND BACKGROUND DATA FOR EACH ELEMENT.

    3 NFSW=1
      NFLAG=0
      DO 2 I=1,N1
      L(I)=-1.
      BK(I)=0.
      PK(I)=0.
    2 K(I)=-1.
    1 IF(NFLAG.EQ.1) GO TO 800

C  FOR STANDARDS ONLY - IF THE TOTAL COUNTS IN A SCALER IS LESS THAN
C  10000, THE MEASUREMENT IS A BACKGROUND, IF IT IS GREATER THAN 10000
C  IT IS A PEAK.
C  ANY SCALER CONTAINING A ZERO IS NOT COUNTED.

      DO 10 I=1,N1
      IF(SC(I).LT.1.) GO TO 10
      IF(SC(I).GT.10000.) GO TO 5
      K(I)=K(I)+1.
      BK(I)=(BK(I)*K(I)+DEADT(SC(I)/SC(NI)*10.))/(K(I)+1.)
      GO TO 10
    5 L(I)=L(I)+1.
      PK(I)=(PK(I)*L(I)+DEADT(SC(I)/SC(NI)*10.))/(L(I)+1.)
   10 CONTINUE
      IF(NSW.EQ.1) GO TO 40
      RETURN
   40 NFLAG=1

C  AFTER ALL STANDARDS HAVE BEEN READ, SUBTRACT THE AVERAGE BACKGROUND
C  FROM THE AVERAGE PEAK FOR EACH ELEMENT.

      DO 20 I=1,N1
   20 PB(I)=PK(I)-BK(I)
      RETURN
  800 IF(NSW.EQ.1) GO TO 15
      GO TO 3

C  COMPUTE THE INTENSITY RATIO FOR EACH ELEMENT.

   15 DO 30 I=1,N1
   30 XK(I)=(DEADT(SC(I)/SC(NI)*10.)-BK(I))/PB(I)*SF(I)
```

```
C  IF INTENSITY RATIOS ARE TO BE ENTERED DIRECTLY, THEY SHOULD BE READ
C  HERE.   TO OBTAIN INTENSITY RATIOS FROM KNOWN CONCENTRATIONS, READ
C  CONCENTRATIONS HERE.

      ES=0.
      DO 500 I=1,N1
      IF(XK(I).LE.0.) XK(I)=0.
  500 ES=ES+XK(I)
      IF(LI(N).NE.0) GO TO 501
      C(N)=1.-ES
      ES=1.
  501 DO 502 I=1,N1
  502 C(I)=XK(I)/ES

C  BEGIN ITERATION FOR COMPUTING CONCENTRATIONS.

C  TO OBTAIN INTENSITY RATIOS FROM KNOWN CONCENTRATIONS, CHANGE
C  THE NEXT STATEMENT TO  NM=3

      DO 550 NM=1,3
      DO 510 I=1,N1
      SS=0.
      RS=0.
      AS=0.
      DO 520 J=1,N
      SS=SS+C(J)*S(J,I)
      RS=RS+C(J)*R(J,I)
  520 AS=AS+C(J)*AC(J,I)
      FCS(I)=1.+H(I)*AS*COSEC+H(I)**2*(AS*COSEC)**2*.05
      W(I)=(R(I,I)*SS)/(S(I,I)*RS)

C  COMPUTE CHARACTERISTIC FLUORESCENCE CORRECTIONS.

      XKF(I)=0.
      DO 530 J=1,N
      IF(KEY(I,J).EQ.0) GO TO 530
      AT=0.
      DO 528 II=1,N
  528 AT=AT+C(II)*FAC(II,J)
      XU=COSEC*AT/AS
      V=(3.33E5/(EO**1.65-EQ(I)**1.65))/AT
      XUV=ALOG(1.+XU)/XU+ALOG(1.+V)/V
      XKF(I)=XKF(I)+C(J)*P(J)*OM(J)/2.*R1(J)*((X(J)-1.)/(Y(I)-1.))**1.67
     1*A(I)/A(J)*FAC(I,J)/AT*XUV
  530 CONTINUE
      IF(XK(I)) 511,511,510
  510 EK=C(I)/W(I)*(1.+XKF(I))*FC(I)/FCS(I)

C  TO OBTAIN INTENSITY RATIOS FROM KNOWN CONCENTRATIONS, INSERT THE
C  TWO STATEMENTS -
C              C(I)=EK
C              GO TO 512
C  COMPUTE CONCENTRATIONS BY ITERATION METHOD ACCORDING TO CRISS.

      C(I)=(XK(I)*C(I)*(1.-EK))/(XK(I)*(C(I)-EK)+EK*(1.-C(I)))
      GO TO 512
  511 C(I)=0.
  512 CONTINUE
      ES=0.
      DO 540 I=1,N1
  540 ES=ES+C(I)
      IF(LI(N).NE.0) GO TO 541
```

```
      C(N)=1.-ES
      ES=1.
  541 IF(NM.EQ.3) GO TO 550
      DO 545 I=1,N
  545 C(I)=C(I)/ES
  550 CONTINUE

C  PRINT RESULTS.

*     CALL ALU(LUTY,IADTTY)
*     CALL OPEN(LUTY,IFDB)
*     IF(IFDB(2).LE.0) CALL ERROR(721,TAB)
*     NW=4
*     CALL RIOS2(0,0,IPRI,$100,LUTY,IADTTY,IS,NW,ISPC)
* 100 SCHENT
*     IF(IS.LE.0) GO TO 650
*     NW=22
      DO 600 I=1,N
      NZ=Z(I)
      IF(N1.EQ.N) GO TO 125
      IF(I.EQ.N) GO TO 130
  125 RFC=1./FCS(I)
      ENCODE(72,706,MESS(2),NC) NZ,XK(I),C(I),RFC
  706 FORMAT(2X,I2,8X,F6.4,5X,F6.4,7X,F6.4)
      GO TO 140
  130 ENCODE(72,707,MESS(2),NC) NZ,C(I)
  707 FORMAT(2X,I2,10X,'N.A. ',4X,F6.4,1X)
*     NW=16
* 140 CALL RIOS2(0,0,IPRI,$110,LUTY,IADTTY,IS,NW,MESS)
* 110 SCHENT
*     IF(IS.LE.0) GO TO 650
  600 CONTINUE
      MESS(2)=CRLF
      ENCODE(72,708,MESS(3),NC) ES
  708 FORMAT(13X,'TOTAL C = ',F6.4,1X)
*     NW=17
*     CALL RIOS2(0,0,IPRI,$120,LUTY,IADTTY,IS,NW,MESS)
* 120 SCHENT

C  CLOSE THE PRINT FILE AND PRINT OUT THE RESULTS.

* 650 CALL CLOSE(LUTY,IFDB)
*     IF (IFDB(2).LE.0) CALL ERROR(721,TAB)
      RETURN
      END
```

# APPENDIX II

## List of Symbols Used in FRAME Program

Variables in FRAME
Subroutine CFCAL

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| A(I) | $A_j$ | Atomic weight of element I |
| A1 | | Intermediate step in computation of backscatter |
| ABCO | | Mass absorption coefficient |
| AC(J,I) | $\mu_A^B$ | Mass absorption coefficient for line of element I in element J |
| AN(IZ) | A | Atomic weight of element whose atomic number is IZ |
| B | | Intermediate step in computation of backscatter |
| BK(I) | | Measured background of element I. |
| C1(M),C2(M),C3(M) | | Coefficients for computing the absorption edge energies |
| COSEC | $\csc\psi$ | Cosecant of the x-ray emergence angle |
| CO | | Variable used in determining if there is a characteristic fluorescence correction |
| CRLF | | Teletype carriage return-line feed |
| E(I) | $E_{q,m}$ | Energy of the measured line of element I |
| EC(M,I) | $E_q$ | Energy of each absorption edge of element I |
| EL(J,I) | $E_{q,m}$ | Energy of each line of element I |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| EO | $E_o$ | Operating kilovoltage |
| EQ(I) | $E_q$ | Energy of the absorption edge of the measured line of element I |
| FAC(J,I) | $\mu_A^B$ | Absorption coefficients needed in characteristic fluorescence correction |
| FC(I) | $1/f(\chi)$, $1/f_p$ | $1/f_p$ of the standard for the pure element I |
| H(I) | | Voltage dependent term in expression for $f_p$ |
| IADTTY | | Address of our teletype (do not use) |
| IBUF(50) | | Input buffer |
| IDUM | | Dummy storage location |
| IFDB(2)<br>IPRI | | Variables needed for our output (do not use) |
| IS | | Error condition of output buffer (applicable to our system) |
| ISPC(4) | | 4 rubouts and 2 carriage return-line feeds on teletype |
| IZ(I) | $Z_j$ | Atomic number of element I as an integer |
| JI | J | Mean ionization potential in Bethe's equation |
| K<br>KK<br>K5 | | Variables in test for characteristic fluorescence correction |
| KEY(J,I) | | The value of this variable defines which characteristic fluorescence corrections have been found |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| L or LI(I) | | Code defining the x-ray lines: 1 = Kα-line, 2 = Lα-line, 3 = Mα-line, 0 = element not analyzed |
| LS | | $L^2$ |
| MESS(40) | | Message array — used for all output |
| MHD(5) | | Date (must be loaded from your computer's clock if you want it) |
| N | | Number of elements in specimen |
| N1 | | Number of elements analyzed |
| NFSW | | NFSW=0 for the initialization of variables needed during the measurement of the standards |
| NW | | Number of characters to be output to the output buffer RIOS2 |
| NYEAR | | The year (1973) |
| NZ | Z | Atomic number |
| OM(I) | $\omega_q$ | Fluorescence yields of elements which excite secondary emission of other elements |
| P(I) | P(k,j) | Parameter in Reed's equation for L→K and K→L fluorescence |
| PB(I) | | Peak intensity - background intensity for the standard for element I |
| IK(I) | | Peak intensity for the standard for element I |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| PST | | Do not use |
| Q | | Intermediate step in computation of backscatter |
| R(J,I) | R | Backscatter factors for radiation I and element J |
| R1(I) | $(\frac{r-1}{r})$ | Jump ratio for characteristic fluorescence correction |
| RFC | $f(\chi)$ | 1/FC(I) |
| S(J,I) | S | Stopping powers |
| SC(I) | | Counts measured in scaler I |
| SETSW TAB | | Do not use |
| U(I) | $E_o/E_q$ | Overvoltage of element I |
| X(I) | $E_o/E_q$ | Overvoltage needed in characteristic fluorescence correction |
| XL(I) | | Number of peak measurements made on standard I |
| XXK(I) | | Number of background measurements made for element I |
| Y(I) | $E_o/E_q$ | Overvoltage of element I |
| Z(I) | $Z_j$ | Atomic number of element I |
| ZL | $\ln(Z_j)$ | Natural log of atomic number |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| C | $C_i^A$ | Coefficient in the expression: $\mu_B^A = C_i^A(\lambda_B)^{n_i^A}$ |
| CN(4) | $n_i^A$ | The value of n in the above expression |
| D1(4),D2(4),D3(4) | | Coefficients for computing the necessary value of C. |
| MI | | Number for selecting the proper coefficients for computing C |

| M | MI |
|---|---|
| 1 | 1 |
| 2 | 2 |
| 3 | 2 |
| 4 | 2 |
| 5 | 3 |
| 6 | 3 |
| 7 | 3 |
| 8 | 3 |
| 9 | 3 |
| 10 | 4 |

| | | |
|---|---|---|
| R(10) | | Energy jump for each edge |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| AS | $\mu_A^*$ | Absorption coefficient of the specimen |
| AT | $\mu_B^*$ | Absorption coefficient needed in characteristic fluorescence correction |
| C(I) | $C_j$ | Concentration of element I |
| EK | $k_j$ | Computed intensity ratio for element I |
| ES | $\Sigma C_j$ | Sum of concentrations |
| FCS(I) | $1/f(\chi)^*, 1/f_p^*$ | Absorption factor, $f_p$ of the specimen for element I |
| K(I) | | Number of times the background is measured for element I |
| L(I) | | Number of times the peak is measured for element I |
| NFLAG | | NFLAG=0 while standards are being measured and =1 while the specimen is being measured |
| NFSW | | NFSW=1 after the first measurement is made on a standard. |
| NSW | | Switch to change from standards (NSW=0) to the specimen (NSW=1) |
| RFC | $f(\chi)^*, f_p^*$ | 1/FCS(I) |
| RS | R* | Backscatter from the specimen |
| SF(I) | | Factors for compound standards |

| Program Variable Name | Common Symbols | Remarks |
|---|---|---|
| SS | $S^*$ | Stopping power for the specimen |
| V | $\left(\frac{3.33 \times 10^5}{E_o^{1.65} - E_q^{1.65}}\right)\left(\frac{1}{\mu_B^*}\right)$ | V term in characteristic fluorescence correction |
| W(I) | $RS^*/SR^*$ | Atomic number factor |
| XK(I) | $k_i$ | Measured intensity ratio for element I |
| XKF(I) | | Characteristic fluorescence factor for element I |
| XU | $\frac{\mu_B^*}{\mu_A^*} \csc\psi$ | u term in characteristic fluorescence correction |
| XUV | | $\frac{\ln(1+u)}{u} + \frac{\ln(1+v)}{v}$ |

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A procedure using a mini-computer for on-line correction of x-ray data from electron microprobe analysis has been developed. This program, called FRAME, allows mass fractions to be computed on-line by the ZAF approach. Besides x-ray intensities, the only input data required are the atomic numbers of the elements present, the analytical line being used, and the operating voltage. Other required parameters such as atomic weights and x-ray mass attenuation coefficients are stored or calculated by the program. FRAME is in FORTRAN IV, and requires about 4K of computer core. Results from FRAME are very close to those of COR2, which is considered to be the most accurate program available for quantitative electron probe microanalysis.



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